

Molecular Mechanics Studies of Acyl Halides: I. Molecular Structures and Conformational Analysis

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ABSTRACT: A new molecular mechanics (MM3) force field has been developed based on various experimental data as well as *ab initio* calculations. Computer-generated molecular structures and energy values were compared with experimentally determined data. The acyl halides studied were formyl halides, acetyl halides, propionyl halides, *n*-butyryl halides, 2-methylpropionyl halides, and 2,2-dimethylpropionyl halides. The rms deviations were 0.005 Å and 1.06° for bond lengths and bond angles, respectively. MM3 was in good overall agreement with the available structural, conformational, and thermodynamic data. © 1998 John Wiley & Sons, Inc. J Comput Chem 19: 1370–1386, 1998

Keywords: acyl halides; MM3; *ab initio* calculations; conformational analysis

Introduction

Molecular mechanics calculations using the MM3 force field¹ have been successfully carried out on a wide variety of organic functional groups including hydrocarbons,² alcohols and ethers,³ amines,⁴ nitro compounds,⁵ sulfides,⁶ phosphine compounds,⁷ aldehydes and ketones,⁸

carboxylic acids,⁹ and carboxylic acid derivatives such as amides¹⁰ and esters.⁸ MM3 is more accurate than its predecessor MM2 in reproducing and predicting most structural features. This present work concentrates on acyl halides, which are closely related to carbonyl compounds, but with substantially different electrostatic and steric effects due to the introduction of halogen atom.

As a starting point for developing an acyl halides MM3 force field, the MM2 parameters¹¹ were scaled to approximate the MM3 parameters. The MM3 force field was then optimized to match empirically derived molecular structures and the experimentally assigned fundamental vibrational frequencies, as well as conformational energies.

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For a more precise treatment, the carbonyl oxygen ($O_{C=O}$) of acyl halides was assigned a new atom type.¹²

In the present work, only saturated acyclic acyl halides¹³ are discussed. For the smaller carbon acyl halides $RCOX$, where R may be any combination of H, CH_3 , or CH_3CH_2 and X may be any halogen (F, Cl, Br, or I), the MM3-calculated properties were compared with results obtained from extensive experimental studies. The molecular structures and conformations that were used for comparisons were determined using standard experimental methods such as electron diffraction, microwave spectroscopy, and vibrational spectroscopy. For the larger acyl halides, the MM3 results were compared primarily with *ab initio* calculations.¹⁴

Results and Discussion

The newly derived MM3 parameters required for calculating accurate molecular structures of acyl halides are presented in Table I. As mentioned earlier, the general MM2 carbonyl oxygen (atom type 7) has been assigned atom type 80 for all acyl halides in an effort to reproduce more precisely the molecular geometries of acyl halides. The $C=O$ stretching force constant parameter, k_s , for the acyl carbonyl group has been increased compared with the corresponding aldehyde and ketone type carbonyl group. This increase in the $C=O$ k_s in acyl halides was necessary to compensate for the strong inductive effect exerted by the electronegative halogen atoms.

The high electronegativity of halogens made it necessary to introduce "secondary electronegativity" correction terms to augment the primary electronegativity correction terms for the bonds attached to the β -positions of an acyl carbonyl carbon. In fact, it was from the studies described herein that led to the addition of a secondary electronegativity correction term. It was highly desirable, however, that this secondary electronegativity correction not require too many adjustable parameters. With this in mind, it was decided to scale the secondary electronegativity effect on one bond according to the primary electronegativity effect on that same bond regardless of the atom type of the α -position of the electronegative atom. For the secondary electronegativity correction, the scaling factor of 0.4 to the primary electronegativity correction term has been included in the MM3

parameter set. The primary electronegativity correction parameters for acyl halides are listed (see Table I), and the primary and secondary electronegativity effects in MM3 are represented in Figure 1.

TABLE I.
MM3 Parameters for Acyl Halides.

(a) Stretching parameters			
Bond type	k_s (mdyn / Å)	l_0 (Å)	
3—80	11.65	1.204	
3—11	4.85	1.382	
3—12	2.88	1.816	
3—13	2.80	1.990	
3—14	2.60	2.218	
(b) Bending parameters			
Angle type	k_b (mdyn · Å / rad ²)	θ_0 (degrees)	
1—3—80	0.32	121.600	
5—3—80	0.32	110.000	
1—3—11	1.95	109.000	
1—3—12	1.45	110.200	
1—3—13	1.18	109.300	
1—3—14	0.97	109.890	
5—3—11	1.34	104.000	
5—3—12	1.22	105.150	
5—3—13	1.12	108.800	
80—3—11	1.75	120.000	
80—3—12	1.24	120.500 (119.680 ^a)	
80—3—13	0.85	120.270 (119.070 ^b)	
80—3—14	0.50	118.400	
0—3—11	1.60		
0—3—12	1.35		
0—3—13	1.05		
0—3—14	1.00		
0—3—80	1.10		
(c) Torsional parameters			
Angle type	V_1 (kcal / mol)	V_2 (kcal / mol)	V_3 (kcal / mol)
1—1—3—11	0.195	0.363	0.143
1—1—3—12	0.977	−0.330	0.321
1—1—3—13	−0.550	−0.146	0.686
1—1—3—14	—	—	—
5—1—3—11	0.000	0.000	0.197
5—1—3—12	0.000	0.000	0.219
5—1—3—13	0.000	0.000	0.195
5—1—3—14	0.000	0.000	0.160

(Continued)

TABLE I.
(Continued)

(d) Primary electronegativity correction parameters

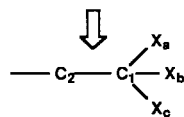
Bond type	End of bond	Atom type	Correction to I_0 (Å)
1—3	3	11	−0.0060
1—3	3	12	−0.0011
1—3	3	13	−0.0005
1—3	3	14	−0.0004
3—5	3	11	−0.0061
3—5	3	12	−0.0057
3—5	3	13	−0.0045
3—5	3	14	—
3—80	3	5	0.0063
3—80	3	11	−0.0184
3—80	3	12	−0.0176
3—80	3	13	−0.0173
3—80	3	14	−0.0154
3—11	3	1	0.0134
3—12	3	1	0.0122
3—13	3	1	0.0106
3—14	3	1	0.0095
3—11	3	80	−0.0332
3—12	3	80	−0.0316
3—13	3	80	−0.0265
3—14	3	80	−0.0199

^aFor formyl chloride.^bFor formyl bromide.

MOLECULAR STRUCTURES

We have derived the required parameters for acyl halides so that MM3 can generate structures of the title compounds to within experimental error limits of the structural data. For each compound where experimental data were available, the calculated molecular geometry was compared with values reported in the literature, preferentially to electron diffraction data (r_g structures, in the gas phase) when the latter were available. Because the moments of inertia were obtained directly from the microwave experiments, the MM3 parameters were developed to reproduce the moments of inertia (r_g) approximately 1% greater than the experimental moments of inertia (r_z) at the expense of molecular geometry, as is appropriate for r_g . The moments of inertia, along with the rotational constants of acyl halides, are shown in Table II. The dipole moments of acyl halides are given in Table S1 (in the Supplementary Material), and the bond moment parameters were the same as MM2.

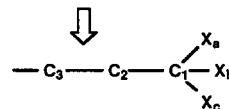
(a) primary electronegativity effect

electronegativity order;
 $X_a > X_b > X_c$

$$\Delta I_e = \Delta I_e(X_a) + (0.62) \Delta I_e(X_b) + (0.62)^2 \Delta I_e(X_c) + \dots$$

$$I_0'(C_1-C_2) = I_0(C_1-C_2) + \Delta I_e$$

(b) secondary electronegativity effect

electronegativity order;
 $X_a > X_b > X_c$

$$\Delta I_e'(X_a) = (0.4) \Delta I_e(X_a),$$

$$\Delta I_e'(X_b) = (0.4) \Delta I_e(X_b),$$

$$\Delta I_e'(X_c) = (0.4) \Delta I_e(X_c).$$

$$\Delta I_e = \Delta I_e'(X_a) + (0.62) \Delta I_e'(X_b) + (0.62)^2 \Delta I_e'(X_c) + \dots$$

$$I_0'(C_2-C_3) = I_0(C_2-C_3) + \Delta I_e$$

FIGURE 1. Primary and secondary electronegativity effects in MM3.

FORMYL FLUORIDE, CHLORIDE, AND BROMIDE

The molecular geometries for formyl halides are shown in Table III. There have been a number of experimental studies on the molecular structure of formyl fluoride. Formyl fluoride was compared with electron diffraction data (r_g),¹⁵ microwave data (r_s),¹⁶ and *ab initio* calculations (r_e). The MM3-calculated molecular structure was within the experimental error for the electron diffraction study. The calculated moments of inertia for formyl fluoride¹⁷ differed from the experimental values about the three principal axes by 0.60%, 0.74%, and 0.56%, respectively.

With the appropriate conversion of the r_z structure to r_g structure, the MM3 formyl chloride geometry was also very close to that in the microwave experiment.^{18b} The calculated moments of inertia about the three principal axes gave differences of 1.06%, 1.10%, and 0.95%, compared with the experimental values.

To our knowledge no structural studies for formyl bromide have been reported. The MM3 force field was able to predict the molecular struc-

TABLE II. Rotational Constants (MHz) and Moments of Inertia ($\text{amu } \text{\AA}^2$)^a of Acyl Halides.^b

(a) Formyl fluoride (HCOF)			
	MW ^c	MM3 (r_g)	% (MM3 – MW ^c)
A	91153.6		
B	11760.0		
C	10396.8		
I_x	5.55	5.5833	0.60
I_y	42.99	43.3088	0.74
I_z	48.62	48.8921	0.56
(b) Formyl chloride (HCOCl)			
	MW ^d	MM3 (r_g)	% (MM3 – MW ^d)
A	77971.4411(53)		
B	6140.8058(4)		
C	5685.2359(4)		
I_x	6.48	6.5485	1.06
I_y	82.32	83.2256	1.10
I_z	88.92	89.7741	0.95
(c) Acetyl fluoride (CH ₃ COF)			
	MW ^e	MM3 (r_g)	% (MM3 – MW ^e)
A	11039.28		
B	9685.65		
C	5322.05		
I_x	45.79	46.1345	0.74
I_y	52.19	52.6869	0.94
I_z	94.99	95.5688	0.61
(d) Acetyl chloride (CH ₃ COCl)			
	MW ^f	MM3 (r_g)	% (MM3 – MW ^f)
A	10162.39		
B	4946.66		
C	3393.07		
I_x	49.75	50.1399	0.78
I_y	102.20	103.0814	0.86
I_z	148.99	149.9645	0.65
(e) Acetyl bromide (CH ₃ COBr)			
	MW ^g	MM3 (r_g)	% (MM3 – MW ^g)
A	10126.35(15)		
B	3027.02(15)		
C	2362.52(15)		
I_x	49.92	50.3715	0.90
I_y	167.01	168.6263	0.97
I_z	213.98	215.7217	0.81

(Continued)

TABLE II.
(Continued)

(f) Acetyl iodide (CH ₃ COI)						
	MW ^h		MM3 (<i>r_g</i>)		% (MM3 – MW ^h)	
A	10137.22					
B	2206.97					
C	1831.48					
<i>I_x</i>	49.87		50.3790		1.02	
<i>I_y</i>	229.06		231.4639		1.05	
<i>I_z</i>	276.02		278.5799		0.93	
(g) Propionyl fluoride (CH ₃ CH ₂ COF)						
	MW ⁱ		MM3 (<i>r_g</i>)		% (MM3 – MW ⁱ)	
	<i>s-trans</i>	<i>gauche</i>	<i>s-trans</i>	<i>gauche</i>	<i>s-trans</i>	<i>gauche</i>
A	10042.63	8701.9				
B	3762.30	3976.9				
C	2832.49	3108.7				
<i>I_x</i>	50.34	58.09	50.8350	58.2484	0.99	0.27
<i>I_y</i>	134.37	127.12	135.0671	127.8413	0.52	0.57
<i>I_z</i>	178.48	162.62	179.4556	164.3614	0.56	1.07
(h) Propionyl chloride (CH ₃ CH ₂ COCl)						
	MW ^j		MM3 (<i>r_g</i>)		% (MM3 – MW ^j)	
	<i>s-trans</i>	<i>gauche</i>	<i>s-trans</i>	<i>gauche</i>	<i>s-trans</i>	<i>gauche</i>
A	8854.770(4)	—				
B	2377.940(1)	—				
C	1918.681(1)	—				
<i>I_x</i>	57.09	—	57.6249	91.6707	0.94	—
<i>I_y</i>	212.59	—	214.2302	162.2273	0.77	—
<i>I_z</i>	263.48	—	265.4206	227.7675	0.73	—

^aThe conversion factor of 5.05531×10^5 MHz / amu Å² is applied for calculating moment of inertia from rotational constant.
^bThe % difference was calculated from the difference of moment of inertia (MM3 [*r_g*] value – MW value) divided by MW value.
^cTaken from ref. 17.
^dTaken from ref. 18b.
^eTaken from ref. 21.
^fTaken from ref. 22.
^gTaken from ref. 23.
^hTaken from ref. 25.
ⁱTaken from ref. 26a.
^jTaken from ref. 29.

ture of formyl bromide. Our computed molecular geometry for formyl bromide was compared with a scaled molecular structure (*r_s*) from *ab initio* calculations (*r_e*) using the RHF/3-21G* basis set (see footnote i of Table III).
From a comparison of the C=O and C—X bond lengths of formyl halides, it was shown that the rms differences are 0.001 Å, 0.005 Å, and 0.007 Å for formyl fluoride, chloride, and bromide, respectively, when compared with the correspond-

ing experimental *r_s* structures (converted from the *r_z* structure of microwave experiment for the chloride and converted from the *r_e* structure of *ab initio* RHF/3-21G* for the bromide).

ACETYL FLUORIDE, CHLORIDE, BROMIDE, AND IODIDE

The molecular structures for these halides are presented in Table IV. Overall, the calculated

TABLE III.
Structural Parameters for Formyl Fluoride, Formyl Chloride, and Formyl Bromide^f (Bond Lengths in Angstroms and Bond Angles in Degrees).

(a) Formyl fluoride (HCOF)							
	ED, r_g^a	ED, r_a^b	MW, r_s^c	MW, r_o^d	<i>Ab initio</i> ^e	MM3	MM3 – ED, r_g^a
$r(\text{C}=\text{O})$	1.188(4)	1.192(11)	1.181(5)	1.183	1.164	1.1867	–0.001
$r(\text{F}—\text{CO})$	1.346(3)	1.351(13)	1.338(5)	1.341	1.314	1.3465	0.001
$r(\text{H}—\text{CO})$	1.108(11)	—	1.095(10)	1.100	1.081	1.1048	–0.003
$\angle(\text{H}—\text{C}=\text{O})$	130 (4)	—	127.3(30)	129	126.94	129.526	–0.47
$\angle(\text{H}—\text{C}—\text{F})$	107.7	—	109.9(30)	108	110.03	107.752	0.05
$\angle(\text{O}=\text{C}—\text{F})$	122.3(2)	121.9(9)	122.8(5)	122.7	123.03	122.723	0.42
rms deviation ^f	(bond length)						0.001
	(bond angle)						0.37
(b) Formyl chloride (HCOCl)							
	Exp., r_g^g	MW, r_s^h	<i>Ab initio</i> ^e	MM3	MM3 – Exp., r_g^g		
$r(\text{C}=\text{O})$	1.1871	1.188(2)	1.165	1.1875	0.000		
$r(\text{Cl}—\text{CO})$	1.7730	1.760(2)	1.756	1.7797	0.007		
$r(\text{H}—\text{CO})$	1.1075	1.0959(3)	1.083	1.1058	–0.002		
$\angle(\text{H}—\text{C}=\text{O})$	126.49(4)	126.48(35)	126.047	127.616	1.13		
$\angle(\text{H}—\text{C}—\text{Cl})$	110.44	109.97(32)	110.699	109.031	–1.41		
$\angle(\text{O}=\text{C}—\text{Cl})$	123.07(1)	123.55	123.255	123.353	0.28		
rms deviation ^f	(bond length)				0.005		
	(bond angle)				1.09		
(c) Formyl bromide (HCOBr)							
	Calculated, r_g^i	MM3	MM3 – calc., r_g^i				
$r(\text{C}=\text{O})$	1.184	1.1851	0.001				
$r(\text{Br}—\text{CO})$	1.948	1.9581	0.010				
$r(\text{H}—\text{CO})$	—	1.1082	—				
$\angle(\text{H}—\text{C}=\text{O})$	126.52	123.915	–2.61				
$\angle(\text{H}—\text{C}—\text{Br})$	109.51	112.383	2.88				
$\angle(\text{O}=\text{C}—\text{Br})$	123.97	123.702	–0.27				
rms deviation ^f	(bond length)		0.007				
	(bond angle)		2.25				

^aTaken from ref. 15.

^bM. E. Jones et al., *J. Am. Chem. Soc.*, **77**, 5278 (1955).

^cTaken from ref. 16.

^dTaken from ref. 17.

^eCalculated at the RHF/6-31G* level, using the Gaussian-90 program (in this work).

^fFor the rms deviation of bond lengths, the C—H bond was excluded. For the rms deviation of bond angles, all angles were included.

^gConverted from the r_z structure [$r(\text{C}=\text{O}) = 1.1853(3)$, $r(\text{C}—\text{Cl}) = 1.7716(2)$, and $r(\text{C}—\text{H}) = 1.0944(3)$] from the microwave experiment (ref. 18b). Scaling done by comparing the r_g structure and the r_z structure calculated from MM3.

^hTaken from ref. 18a.

ⁱConverted from the r_e structure [$r(\text{C}=\text{O}) = 1.1857$, $r(\text{C}—\text{Br}) = 1.9241$, and $r(\text{C}—\text{H}) = 1.0757$] from the *ab initio* RHF/3-21G* method (Gaussian-94 program, in this work). The scaling is done by comparing the r_g structure from the electron diffraction experiment (ref. 21) and the r_e structure from *ab initio* RHF/3-21G* method of acetyl bromide [$r_g(\text{C}=\text{O}) - r_e(\text{C}=\text{O}) = -0.002$, $r_g(\text{C}—\text{Br}) - r_e(\text{C}—\text{Br}) = 0.024$, and $r_g(\text{C}—\text{C}(\text{O})) - r_e(\text{C}—\text{C}(\text{O})) = 0.015$].

TABLE IV.
Structural Parameters for Acetyl Fluoride, Acetyl Chloride, Acetyl Bromide, and Acetyl Iodide (Bond Lengths in Angstroms and Bond Angles in Degrees).

(a) Acetyl fluoride (CH ₃ COF)							
	ED, r_g^a	MW, r_g^b	<i>Ab initio</i> ^c	<i>Ab initio</i> ^d	MM3	MM3 – ED ^a	
$r(\text{C}=\text{O})$	1.185(2)	1.181(10)	1.168	1.168	1.1848	0.000	
$r(\text{F}-\text{CO})$	1.362(2)	1.348(15)	1.326	1.326	1.3583	−0.004	
$r(\text{C}-\text{CO})$	1.505(2)	1.503(3)	1.495	1.496	1.5037	−0.001	
$r(\text{C}-\text{H})_{\text{av}}$	1.101(4)	1.091	1.083	1.082	1.1067	0.006	
$\angle(\text{C}-\text{C}=\text{O})$	128.8	128.35(100)	128.46	128.53	128.799	0.00	
$\angle(\text{C}-\text{C}-\text{F})$	110.5(5)	110.3(10)	110.94	110.88	110.319	−0.18	
$\angle(\text{O}=\text{C}-\text{F})$	120.7(4)	121.35	120.60	121.06	120.882	0.18	
$\angle(\text{CO}-\text{C}-\text{H})_{\text{av}}$	—	109.30	109.48	109.53	110.897	—	
$\angle(\text{H}-\text{C}-\text{H})_{\text{av}}$	109.3(6)	109.66	109.46	109.40	108.008	−1.29	
rms deviation ^e	(bond length)					0.002	
	(bond angle)					0.15	
(b) Acetyl chloride (CH ₃ COCl)							
	ED, r_g^f	MW + ED, r_z^f	MW, r_s^g	MW, r_0^h	<i>Ab initio</i> ^d	MM3	MM3 – ED ^f
$r(\text{C}=\text{O})$	1.187(3)	1.185(3)	1.185(5)	1.192(10)	1.167	1.1860	−0.001
$r(\text{Cl}-\text{CO})$	1.798(3)	1.796(2)	1.796(5)	1.789(5)	1.785	1.7959	−0.002
$r(\text{C}-\text{CO})$	1.508(5)	1.505(3)	1.501(6)	1.499(10)	1.503	1.5105	0.003
$r(\text{C}-\text{H})_{\text{av}}$	1.092(5)	1.092(5)	1.095(2)	1.083(5)	1.082	1.1070	0.015
$\angle(\text{C}-\text{C}=\text{O})$	127.5(9)	127.2	127.4(5)	127.08(17)	127.12	126.815	−0.69
$\angle(\text{C}-\text{C}-\text{Cl})$	112.2(9)	111.6(6)	111.2(1)	112.65(50)	112.81	111.950	−0.25
$\angle(\text{O}=\text{C}-\text{Cl})$	120.3(6)	121.2(5)	121.4	120.27	120.07	121.235	0.94
$\angle(\text{CO}-\text{C}-\text{H})_{\text{av}}$	—	—	109.2	110.35(17)	109.37	111.005	—
$\angle(\text{H}-\text{C}-\text{H})_{\text{av}}$	108.8(8)	108.8(8)	108.9	—	109.57	107.894	−0.91
rms deviation ^e	(bond length)						0.002
	(bond angle)						0.69
(c) Acetyl bromide (CH ₃ COBr)							
	ED, r_g^f	MW + ED, r_z^f	<i>Ab initio</i> ⁱ		MM3	MM3 – ED ^f	
$r(\text{C}=\text{O})$	1.184(3)	1.181(3)	1.186		1.1862	0.002	
$r(\text{Br}-\text{CO})$	1.977(3)	1.974(3)	1.953		1.9740	−0.003	
$r(\text{C}-\text{CO})$	1.519(3)	1.516(3)	1.504		1.5110	−0.008	
$r(\text{C}-\text{H})_{\text{av}}$	—	—	1.082		1.1100	—	
$\angle(\text{C}-\text{C}=\text{O})$	127.1	126.7	128.09		126.918	−0.18	
$\angle(\text{C}-\text{C}-\text{Br})$	111.0(15)	111.0(15)	111.13		111.702	0.70	
$\angle(\text{O}=\text{C}-\text{Br})$	121.9(15)	122.3(15)	120.79		121.380	−0.52	
$\angle(\text{CO}-\text{C}-\text{H})_{\text{av}}$	—	—	109.36		110.033	—	
$\angle(\text{H}-\text{C}-\text{H})_{\text{av}}$	109.5(11)	109.9(11)	109.58		107.864	−1.64	
rms deviation ^e	(bond length)					0.005	
	(bond angle)					0.51	

(Continued)

TABLE IV.
(Continued)

(d) Acetyl iodide (CH ₃ COI)				
	ED, r_g^j	MW + ED, r_z^j	MM3	MM3 – ED ^j
$r(\text{C}=\text{O})$	1.198(13)	1.194(13)	1.1880	–0.010
$r(\text{I}—\text{CO})$	2.217(15)	2.214(9)	2.2062	–0.011
$r(\text{C}—\text{CO})$	1.492(15)	1.489(15)	1.5101	0.018
$r(\text{C}—\text{H})_{\text{av}}$	1.101(4)	1.088(4)	1.1079	0.007
$\angle(\text{C}—\text{C}=\text{O})$	128.8	128.8	127.028	–1.78
$\angle(\text{C}—\text{C}—\text{I})$	111.7(9)	111.7(9)	112.613	0.91
$\angle(\text{O}=\text{C}—\text{I})$	119.5(8)	119.5(8)	120.359	0.86
$\angle(\text{CO}—\text{C}—\text{H})_{\text{av}}$	—	—	110.968	—
$\angle(\text{H}—\text{C}—\text{H})_{\text{av}}$	110.8(8)	110.8(8)	107.932	–2.87
rms deviation ^e	(bond length)			0.013
	(bond angle)			1.26

^aTaken from ref. 19.^bTaken from ref. 20.^cRHF/5-31G** level [V. J. Klimkovski, et al., *J. Comput. Chem.*, **5**, 517 (1984)].^dCalculated at the RHF/6-31G* level, using the Gaussian-90 program (in this work).^eFor the rms deviation of bond length, the C—H bond was excluded. For the rms deviation of bond angle, those angles containing hydrogen were excluded.^fTaken from ref. 21.^gTaken from ref. 32.^hTaken from ref. 22.ⁱCalculated at the RHF/3-21G* level, using the Gaussian-94 program (in this work).^jTaken from ref. 24.

structures are in agreement with the experimental values (the r_g structural data). The structure of acetyl fluoride has been studied with electron diffraction¹⁹ and microwave²⁰ methods, and the structure was well reproduced by molecular mechanics. The calculated moments of inertia of acetyl fluoride were 0.74%, 0.94%, and 0.61% different from the experimental moments of inertia determined by Pierce et al.²⁰

Electron diffraction²¹ and microwave²² studies on the molecular structure of acetyl chloride have been reported. For comparison of the molecular geometry, the electron diffraction data obtained by Tsuchiya et al.²¹ were used, and our calculated structure was within the experimental error. The calculated moments of inertia of acetyl chloride were larger by 0.78%, 0.86%, and 0.65%, compared with experimental values determined by Sinnott.²²

The molecular structure of acetyl bromide was also well reproduced by MM3, compared with the structures by the electron diffraction method.²¹ The calculated moments of inertia were within 1%

(differences of 0.90%, 0.97%, and 0.81%, respectively) of the experimental moments determined by Krisher.²³

The molecular structure of acetyl iodide was also calculated by MM3 and compared with the structure determined by electron diffraction experiment.²⁴ The percent differences of the moments of inertia were 1.02%, 1.05%, and 0.93% from the experimental moments determined by Moloney and Krisher.²⁵

It was found that the *ab initio* values (r_e) using the 6-31G* basis set for the acetyl fluoride and acetyl chloride C=O bond lengths were approximately 0.02 Å shorter than the distances from either electron diffraction (r_g) or MM3, whereas the 3-21G* calculations indicate that the C=O bond length for acetyl bromide was approximately the same as the electron diffraction or MM3 values. The calculated molecular structures of acetyl fluoride, acetyl chloride, acetyl bromide, and acetyl iodide were fit well to the electron diffraction results,^{19,21,24} and gave rms differences of 0.002 Å and 0.15°, 0.002 Å and 0.69°, 0.005 Å and 0.51°, and

0.013 Å and 1.26°, respectively, for the bond lengths (excluding C—H bonds) and bond angles (excluding angles containing H).

PROPIONYL FLUORIDE, CHLORIDE, AND BROMIDE

The molecular structures for the propionyl halides are presented with the values of the rms differences for the bond lengths (excluding C—H bonds) and bond angles (excluding angles containing hydrogen) in Table V. No electron diffraction data for propionyl fluoride were found. Two microwave studies were reported for propionyl fluoride.^{26a,27} The molecular mechanics-derived structure of the *s-trans* conformer was compared with those (after converting the r_s structures from microwave spectroscopy²⁷ to an r_g basis). MM3 yielded similar geometries for both the *s-trans* and *gauche* conformers of propionyl fluoride, with a single exception: the C₂—C₃ bond length of *s-trans*-propionyl fluoride was 0.011 Å shorter than that of *gauche*-propionyl fluoride as seen from both the microwave experiment^{26a} (0.008 Å) and *ab initio* calculations (0.009 Å). Molecular mechanics calculations and *ab initio* calculations showed little change in angles around the acyl group in going from *s-trans* to *gauche* conformer, whereas the microwave experiment^{26a} showed dramatic changes (see Table V). The percent differences of the our calculated moments of inertia of three principal axes from the experiment^{26a} were 0.99%, 0.52%, and 0.56% for *s-trans*-propionyl fluoride, and were 0.27%, 0.57%, and 1.07% for *gauche*-propionyl fluoride, respectively.

For propionyl chloride, one electron diffraction study²⁸ and two microwave studies^{29,30} have been found. Again, there was good agreement between the structure of propionyl chloride from the electron diffraction study²⁸ and the molecular structure for the MM3 Boltzmann distribution. The ratio of *s-trans* and *gauche* isomers was 84% and 16%. The percent differences of the calculated moments of inertia (r_g) of *s-trans*-propionyl chloride for three principal axes were 0.94%, 0.77%, and 0.73%, respectively, above the experimental values.²⁹

Our calculated molecular structure for propionyl bromide was very close to the structure from an electron diffraction study by Skjørholm and Hagen.³¹ MM3 and *ab initio* RHF/3-21G* level calculations on propionyl bromide showed that the molecular geometry of the *gauche* conformer was almost the same as that of the *s-trans* conformer,

as observed previously for both propionyl fluoride and propionyl chloride.

LARGER ACYL HALIDES

It is very straightforward to calculate the molecular structures of acyl halides larger than the propionyl halides inasmuch as no additional parameters need to be fixed. For *n*-butyryl halides, 2-methylpropionyl halides, and 2,2-dimethylpropionyl halides, all of the parameters required have already been determined based on the formyl, acetyl, and propionyl halides, to within experimental errors (see Supplementary Material).

CONFORMATIONAL ANALYSIS

To properly investigate the conformations of acyl halides with molecular mechanics, it is essential to obtain accurate torsional potentials. The MM3 force field uses a three-term Fourier series to describe the torsional contributions to the total energy. There are three parameters, V_1 , V_2 , and V_3 , required for each unique dihedral angle. For each of the acyl halide series studied, we began by developing the torsion angle $\omega(\text{H—C}_{\text{sp}^3}\text{—C}_\text{C}=\text{O—X})$ (torsion angle types 5—1—3—11, 5—1—3—12, 5—1—3—13, and 5—1—3—14, respectively) according to the experimental barriers (1039–1305 cal/mol) to internal rotation of the methyl group in acetyl halides^{20,21b,22,24,25} (see the subsection “Barrier to Internal Rotation of Methyl Group of Propionyl Halides”). Because the torsional potential energy curves of the barrier to internal rotation of acetyl halides show perfect threefold symmetry, only a V_3 term was necessary. For propionyl halides, a combination of V_1 , V_2 , and V_3 torsional terms for the torsion angle $\omega(\text{C}_{\text{sp}^3}\text{—C}_{\text{sp}^3}\text{—C}_\text{C}=\text{O—X})$ (torsional angle types 1—1—3—11, 1—1—3—12, and 1—1—3—13, respectively) had to be used. The V_1 and V_2 terms for these torsional angles played important roles in determining the structural characteristics of acyl halide compounds. For example, these torsional parameters affected all the torsion angles $\omega(\text{C}_{\text{sp}^3}\text{—C}_{\text{sp}^3}\text{—C}_\text{C}=\text{O—X})$, the conformational ratio of stable conformers, and the distribution between each component of the moments of inertia. This was particularly evident for the *gauche* forms of propionyl halides. Despite the fact that the acyl halide carbonyl oxygen atom type was defined differently from the aldehyde or ketone carbonyl oxygen atom type, the V_1 , V_2 , and V_3 torsional parameters related to aldehyde or ketone carbonyl group [tor-

TABLE V.
Structural Parameters for Propionyl Fluoride, Propionyl Chloride, and Propionyl Bromide (Bond Lengths in Angstroms and Bond Angles in Degrees).

(a) Propionyl fluoride (CH ₃ CH ₂ COF)								
	Exp., <i>r_g</i>		<i>Ab initio</i> ^d		MM3		MM3 – exp.	
	<i>s-trans</i> ^{a, c}	<i>gauche</i> ^{b, c}	<i>s-trans</i>	<i>gauche</i>	<i>s-trans</i>	<i>gauche</i>	<i>s-trans</i>	<i>gauche</i>
<i>r</i> (C=O)	1.185	1.193	1.169	1.169	1.1849	1.1849	0.000	–0.008
<i>r</i> (C – F)	1.362	1.352	1.327	1.328	1.3640	1.3637	0.002	0.012
<i>r</i> (C ₁ – C ₂) ^f	1.507	1.509	1.501	1.501	1.5083	1.5079	0.001	–0.001
<i>r</i> (C – H) _{av}	1.096	1.104	1.084	1.084	1.1107	1.1099	0.007	0.006
<i>r</i> (C ₂ – C ₃)	1.552 ^e	1.542	1.524	1.533	1.5179	1.5292	–0.034	–0.013
∠(C – C=O)	128.4	126.7(5)	128.70	128.49	129.270	128.588	0.87	1.89
∠(C – C – F)	110.0	110.9(2)	110.86	111.37	110.122	110.571	0.12	–0.33
∠(O=C – F)	121.6	122.4	120.45	120.24	120.609	120.833	–0.99	–1.57
∠(C ₁ – C ₂ – C ₃)	113.0	112.5	112.96	112.46	112.631	112.520	–0.37	0.02
∠(CO – C – H) _{av}	109.5	107.4	107.15	107.37	109.323	109.203	–0.18	1.80
∠(C ₃ – C ₂ – H) _{av}	—	—	111.66	110.60	109.245	109.466	—	—
∠(C ₂ – C ₃ – H) _{av}	109.2	110.7	111.04	110.69	111.576	111.582	2.38	0.88
∠(H – C ₂ – H)	106.4	108.2	105.90	108.26	106.909	106.502	0.51	–1.70
∠(H – C ₃ – H) _{av}	108.6	108.4	108.20	108.22	107.286	107.280	–0.31	–1.12
∠(C – C – C=O)	0.0	119.9(22)	–0.2	127.1	0.0	122.2	0.0	2.3
rms deviation ^g	(bond length)						0.001	0.010
	(bond angle)						0.69	1.24
(b) Propionyl chloride (CH ₃ CH ₂ COCl)								
	Exp., <i>r_g</i> ^h	MW, <i>r_s</i>		<i>Ab initio</i> ^d		MM3 ^k	MM3 – exp. ^h	
		<i>s-trans</i> ⁱ	<i>s-trans</i> ^j	<i>s-trans</i>	<i>gauche</i>			
<i>r</i> (C=O)	1.188	1.187	1.201	1.168	1.168	1.1861	–0.002	
<i>r</i> (C – Cl)	1.797	1.792(8)	1.789	1.788	1.789	1.8017	0.005	
<i>r</i> (C ₁ – C ₂) ^f	1.527	1.528(9)	1.509	1.508	1.509	1.5153	–0.012	
<i>r</i> (C – H) _{av}	1.125	1.087	1.092	1.084	1.083	1.1108	–0.014	
<i>r</i> (C ₂ – C ₃)	1.525	1.514(8)	1.523	1.525	1.534	1.5271	0.002	
∠(C – C=O)	127.0(7)	127.6(9)	126.4	127.43	126.78	127.271	0.27	
∠(C – C – Cl)	112.1(4)	112.0(4)	112.3	112.70	113.55	111.831	–0.27	
∠(O=C – Cl)	120.9	120.4	121.3	119.99	119.67	120.895	0.01	
∠(C ₁ – C ₂ – C ₃)	112.7(7)	112.0(8)	112.7	112.08	112.23	112.545	–0.16	
∠(CO – C – H) _{av}	102.0(4.1)	107.4	—	107.44	107.34	109.528	7.53	
∠(C ₃ – C ₂ – H) _{av}	—	—	—	111.66	110.48	109.105	—	
∠(C ₂ – C ₃ – H) _{av}	109.6(23)	111.4	110.0	110.65	110.62	111.568	1.97	
∠(H – C ₂ – H)	105.3(9.8)	106.2	106.4	106.24	108.83	106.864	1.56	
∠(H – C ₃ – H) _{av}	—	107.9	108.6	108.27	108.29	107.295	—	
∠(C – C – C=O) ^l	0.0	0.0	0.0	0.0		0.0	0.0	
∠(C – C – C=O) ^m	120.0(7)				106.5	105.6	–14.4	
rms deviation ^g	(bond length)						0.007	
	(bond angle)						0.21	

(Continued)

TABLE V.
(Continued)

(c) Propionyl bromide (CH ₃ CH ₂ COBr)					
	Exp., <i>r_g</i> ⁿ	<i>Ab initio</i> ^o		MM3 ^p	MM3 – exp. ⁿ
		<i>s-trans</i>	<i>gauche</i>		
<i>r</i> (C=O)	1.183	1.186	1.186	1.1863	0.003
<i>r</i> (C—Br)	1.980	1.954	1.958	1.9795	–0.001
<i>r</i> (C ₁ —C ₂) ^f	1.525	1.508	1.508	1.5159	–0.009
<i>r</i> (C—H) _{av}	1.115	1.083	1.082	1.1117	–0.003
<i>r</i> (C ₂ —C ₃)	1.526	1.535	1.546	1.5286	0.003
∠(C—C=O)	126.6(6)	127.64	128.01	127.170	0.57
∠(C—C—Br)	112.5(4)	111.53	111.64	111.868	–0.63
∠(O=C—Br)	120.9	120.83	120.35	120.960	0.06
∠(C ₁ —C ₂ —C ₃)	111.8(9)	111.18	110.86	112.650	0.85
∠(CO—C—H) _{av}	—	107.65	109.39	109.541	—
∠(C ₃ —C ₂ —H) _{av}	—	111.51	110.22	109.114	—
∠(C ₂ —C ₃ —H) _{av}	—	110.44	110.17	111.590	—
∠(H—C ₂ —H)	—	107.12	109.71	106.696	—
∠(H—C ₃ —H) _{av}	108.6	108.48	108.77	107.271	–1.33
∠(C—C—C=O) ^l	0	0.0		0.0	0.0
∠(C—C—C=O) ^m	105(15)		108.1	110.7	5.7
rms deviation ^q	(bond length)				0.005
	(bond angle)				0.60

^aConverted from the *r_s* structure [*r*(C=O) = 1.181, *r*(C—F) = 1.348, *r*(C₁—C₂) = 1.505, *r*(C₂—C₃) = 1.550, and *r*(C—H)_{av} = 1.086] from the microwave experiment (ref. 27).
^bConverted from the *r_s* structure [*r*(C=O) = 1.189, *r*(C—F) = 1.338(9), *r*(C₁—C₂) = 1.507, *r*(C₂—C₃) = 1.539(11), and *r*(C—H)_{av} = 1.094] from the microwave experiment (ref. 26a).
^cScaling done by comparing the *r_g* structure from the electron diffraction experiment (ref. 19) and the *r_s* structure from the microwave experiment (ref. 20) of acetyl fluoride [*r_g*(C=O) – *r_s*(C=O) = 0.004, *r_g*(C—F) – *r_s*(C—F) = 0.014, *r_g*(C—C) – *r_s*(C—C) = 0.002, and *r_g*(C—H) – *r_s*(C—H) = 0.010].
^dCalculated at the RHF/6-31G* level, using the Gaussian-90 program (in this work).
^eThis value of *r_s*(C₂—C₃) appeared to be poorly determined, so this bond was not used in calculating the rms deviation for the bond length.
^fNumbering of carbons is C₃—C₂—C₁=O.
^gFor the rms deviation of bond length, the C—H bond was excluded. For the rms deviation of bond angles, angles containing hydrogen were excluded.
^hConverted from the *r_a* structure [*r*(C=O) = 1.187(5), *r*(C—Cl) = 1.795(5), *r*(C₁—C₂) = 1.525(15), *r*(C₂—C₃) = 1.523(16), and *r*(C—H) = 1.107(11)] from the electron diffraction experiment (ref. 28). The ratio of *s-trans*:*gauche* is 76.5:23.5 at 293 K. The scaling was done by comparing the *r_g* structure and the *r_a* structure calculated from MM3.
ⁱTaken from ref. 30.
^jTaken from ref. 29.
^kThe ratio of *s-trans*:*gauche* is 83.9:16.1 at 298 K.
^lFor the *s-trans* conformer.
^mFor the *gauche* conformer.
ⁿConverted from the *r_a* structure [*r*(C=O) = 1.182(5), *r*(C—Br) = 1.979(5), *r*(C₁—C₂) = 1.523(4), *r*(C₂—C₃) = 1.524(11), and *r*(C—H) = 1.109(9)] from the electron diffraction experiment (ref. 31). The ratio of *s-trans*:*gauche* is 71:29 at 293 K. The scaling is done by comparing the *r_g* structure and the *r_a* structure calculated from MM3.
^oCalculated at the RHF/3-21G* level, using the Gaussian-94 program (in this work).
^pThe ratio of *s-trans*:*gauche* is 63:37 at 298 K.

sional parameters for the torsion angles $\omega(\text{H}-\text{C}_{\text{sp}^3}-\text{C}=\text{O})$ and $\omega(\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}-\text{C}=\text{O})$ have not been changed for acyl halide carbonyl group.

TORSIONAL POTENTIAL FUNCTIONS OF ACYL HALIDES

The stable conformations of the acyl halides are shown in Figure 2. It is well known that, for acetyl halides, the *syn* (or *cis*) conformer (where H is in the symmetry plane eclipsing the C=O bond) is the most stable conformation, whereas the *anti* (or *trans*) conformer (where H is in the symmetry plane eclipsing the C—X bond) has the least stable conformation.^{19–24,32}

It is well known that propionyl halides exist as two stable conformers, *s-trans* and *gauche*, and

that the *s-trans* conformer (terminal methyl group in the plane of the symmetry eclipsing C=O) is more stable than the *gauche* (terminal methyl group *gauche* to halide atom). The energy differences between the stable conformers, and other energy parameters for propionyl halides, are listed in Table VI.

For propionyl fluoride, the energy difference between the *gauche* and the *s-trans* forms has been determined from a microwave experiment²⁷ ($\Delta E^0 = 1290$ cal/mol), and also from gas phase IR ($\Delta H^0 = 1280$ cal/mol^{26a} or 1240 cal/mol³³). The energy barriers were 2100 cal/mol (from *s-trans* to *gauche*), and 800 cal/mol (from the *gauche* to the *gauche* form), respectively.^{26a} MM3 correctly reproduced these energy differences ($\Delta H^0 = 1295$ cal/mol and $\Delta E^0 = 1247$ cal/mol). The molecular mechanics energy difference between the

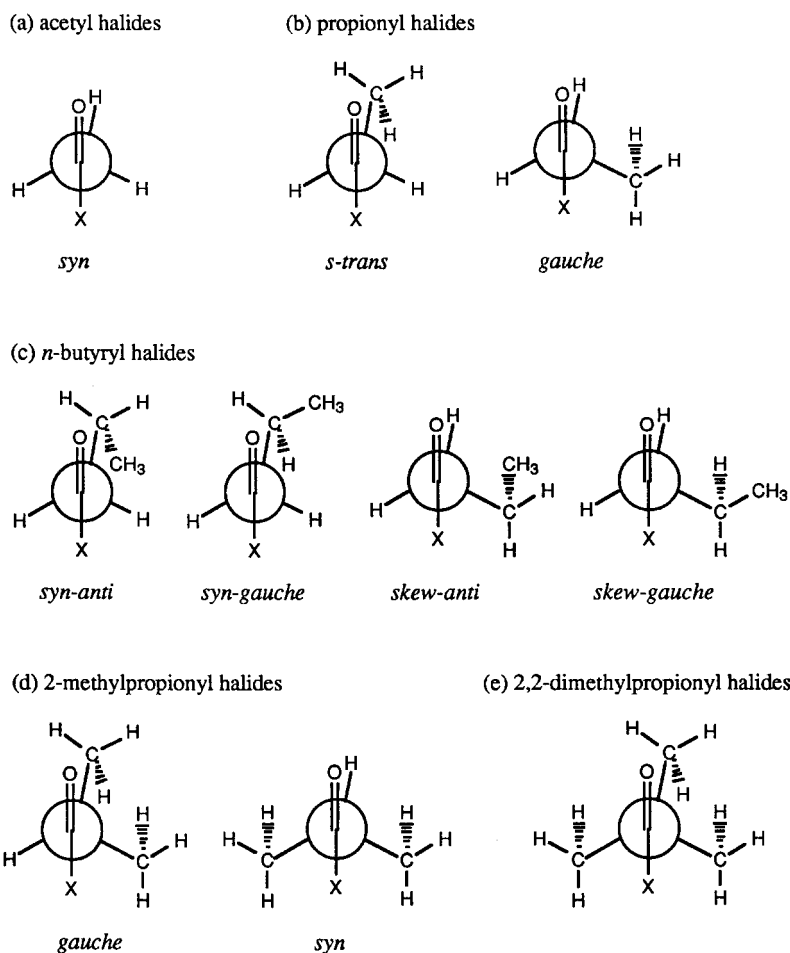


FIGURE 2. Stable conformations^a of acyl halides (X=F, Cl, Br, or I). Defining the conformations, except for propionyl halides, was decided exclusively by referring to the carbonyl group.

TABLE VI.
Energy Parameters and Energy Values (Calories per Mole) for Propionyl Fluoride, Propionyl Chloride, and Propionyl Bromide (Experiment, *Ab initio*, and MM3).

(a) Propionyl fluoride				
Energy parameter	MW ^{a, b}	IR ^{c, d}	<i>Ab initio</i> ^c RHF / 6-31G*	MM3 ^e
ΔH^\ddagger (<i>s-trans</i> \rightarrow <i>gauche</i>)	2100	2060(20)	2027	1978
ΔH^\ddagger (<i>gauche</i> \rightarrow <i>gauche</i>)	800	850(20)	1075	957
ΔH^0 (<i>gauche</i> – <i>s-trans</i>)		1280(5)		1295
		760(30) ^f		
ΔE^0 (<i>gauche</i> – <i>s-trans</i>)	1290(50)		1018	1247
ΔG^0 (<i>gauche</i> – <i>s-trans</i>)				672
(b) Propionyl chloride				
Energy parameter	IR ^{g, d}	ED ^h	<i>Ab initio</i> ^c RHF / 6-31G*	MM3 ^e
ΔH^\ddagger (<i>s-trans</i> \rightarrow <i>gauche</i>)	2170(20)		2092	1921
ΔH^\ddagger (<i>gauche</i> \rightarrow <i>gauche</i>)	2930(110)		1956	3110
ΔH^0 (<i>gauche</i> – <i>s-trans</i>)	1400(230)	1430(480)		1456
	1700(130) ⁱ			
ΔE^0 (<i>gauche</i> – <i>s-trans</i>)			1381	1389
ΔG^0 (<i>gauche</i> – <i>s-trans</i>)				898
(c) Propionyl bromide				
Energy parameter	IR ^{j, d}	ED ^k	<i>Ab initio</i> ^l RHF / 3-21G*	MM3 ^e
ΔH^\ddagger (<i>s-trans</i> \rightarrow <i>gauche</i>)	2030(20)		2726	2032
ΔH^\ddagger (<i>gauche</i> \rightarrow <i>gauche</i>)	3200(170)		2883	3124
ΔH^0 (<i>gauche</i> – <i>s-trans</i>)	720(280)	1310(600)		813
	1150(80) ⁱ			
ΔE^0 (<i>gauche</i> – <i>s-trans</i>)			1334	729
ΔG^0 (<i>gauche</i> – <i>s-trans</i>)				320

^aTaken from ref. 27.
^bFrom the measured microwave spectrum for torsional vibrational modes of *s-trans* and *gauche* forms.
^cTaken from ref. 26a.
^dCalculated from the torsional potential function formulated from the gas-phase IR frequencies of *s-trans* and *gauche* forms for the asymmetric torsional transitions.
^eFor MM3, the values are calculated by changing the dihedral angle around central C—C bond (C—C—C=O) from 0° (the most stable *s-trans* conformer) to 180° (the *s-cis* conformer) in 10° increment with the optimized structural parameters of the most stable form. The resulting conformers and the transition states are thus fully minimized. ΔE^0 was obtained from the final energy difference between the corresponding stable conformers. ΔH^0 and ΔS^0 were obtained from the thermodynamic part of MM3 output, and ΔG^0 was obtained from the ΔH^0 and ΔS^0 at 298 K using the thermodynamic equation, $\Delta G^0 = \Delta H^0 - T\Delta S^0$. ΔH^\ddagger was estimated to be equal to the final steric energy difference between the corresponding ground state and transition state.
^fDetermined from the temperature-dependent liquid-phase Raman spectrum.
^gTaken from ref. 30.
^hTaken from ref. 28.
ⁱDetermined from the temperature-dependent gas-phase Raman spectrum.
^jTaken from ref. 34.
^kTaken from ref. 31.
^lUsing the Gaussian-94 program (in this work).

s-trans and *gauche* form, the energy barriers from *s-trans* to *gauche* form, and from the *gauche* to the *gauche* form were 1247, 1978, and 957 cal/mol, respectively.

For propionyl chloride, the energy difference between the *gauche* and the *s-trans* forms has been determined from gas phase IR ($\Delta H^0 = 1400$ cal/mol³⁰ or 840 cal/mol^{26b}) and from electron diffraction experiments²⁸ ($\Delta H^0 = 1430$ cal/mol). The energy barriers of 2170 cal/mol (from *s-trans* to *gauche*) and 2930 cal/mol (from the *gauche* to the *gauche* forms) were also determined from the gas phase IR study.³⁰ Again, MM3 correctly gave the energy difference between *s-trans* and *gauche* forms ($\Delta H^0 = 1456$ cal/mol), and the energy barriers from *s-trans* to *gauche* forms and the interconversion of the *gauche* to *gauche* forms (1921 and 3110 cal/mol, respectively).

For propionyl bromide, the energy difference between the *gauche* and the *s-trans* forms has been determined from gas phase IR ($\Delta H^0 = 720$ cal/mol³⁴ and 1040 cal/mol^{26b}) and electron diffraction experimentation³¹ ($\Delta H^0 = 1310$ cal/mol). The energy barriers were 2030 cal/mol (from the *s-trans* to the *gauche* form) and 3200 cal/mol (from the *gauche* to the *gauche*) from the gas phase IR spectra.³⁴ Our calculated energy difference between the *s-trans* and *gauche* forms were 813 cal/mol (ΔH^0). The energy barriers from the *s-trans* to *gauche* and from the *gauche* to the *gauche* were 2032 and 3124 cal/mol, respectively.

BARRIER TO INTERNAL ROTATION OF METHYL GROUP OF PROPIONYL HALIDES

The calculated barriers to internal rotation of the methyl group of acyl halides are summarized in Table VII. From the splitting of the internal rotational transitions of the terminal methyl group in the rotational spectroscopic experiments, the threefold barriers [$\text{H}-\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}-\text{C}(=\text{O})$] have been determined. For acetyl halides, MM3 torsional parameters for $\text{H}-\text{C}-\text{C}-\text{X}$ torsional angles were fixed to match exactly the experimental values (for acetyl fluoride, 1041 cal/mol²⁰ and 1039 cal/mol¹⁹; for acetyl chloride, 1296 cal/mol²², 1260 cal/mol,^{21b} and 1284 cal/mol³⁵; for acetyl bromide, 1305 cal/mol²³ and 1256 cal/mol^{21b}; and for acetyl iodide, 1301 cal/mol²⁵). All of these methyl group barriers to internal rotation in acetyl halides were similar to that of acetaldehyde (1143 cal/mol³⁶ or 1233 cal/mol³⁷), and they were much larger than that of acetone (778 cal/mol).³⁸

Our calculations for the barriers to internal rotation of the methyl group of the *s-trans* conformers of propionyl halides showed close agreement with the experimental values. For the *s-trans* conformation of propionyl fluoride the barrier to internal rotation of the methyl group was determined from the microwave spectrum to be 2400 cal/mol by Stiefvater et al.²⁷ and from the far infrared spectrum to be 2670 cal/mol by Guirgis et al.³³ Our calculated barrier to internal rotation of the methyl group for propionyl fluoride was 2828 cal/mol, whereas RHF/6-31G* calculations provided 2743 cal/mol. For the *s-trans* conformation of propionyl chloride, the values of 2480 cal/mol by Karlsson²⁹ and 2500 cal/mol by Mata and Alonso³⁹ for the barrier to internal rotation of the methyl group were determined from the microwave spectrum. From the far infrared spectrum, Durig et al.³⁰ reported a barrier of 2720 cal/mol. The molecular mechanics values for propionyl chloride was 2863 cal/mol, whereas *ab initio* RHF/6-31G* calculations provided 2913 cal/mol. For the *s-trans* conformation of propionyl bromide, the barrier to internal rotation of the methyl group was determined to be 2510 cal/mol by Frankiss et al.^{26b} and 2690 cal/mol by Durig et al.³⁴ Our calculated barrier was 2858 cal/mol, whereas *ab initio* RHF/3-21G* level calculations gave 2308 cal/mol.

The barriers to internal rotation of the methyl group of the *gauche* conformer of propionyl halides have not been determined successfully from either microwave or IR spectroscopy studies. MM3 predicted 2404, 2284, and 2242 cal/mol for methyl group of the *gauche* conformer of propionyl fluoride, propionyl chloride, and propionyl bromide, respectively; whereas RHF/6-31G* level calculations for propionyl fluoride and propionyl chloride, and *ab initio* RHF/3-21G* level calculations for propionyl bromide provided 3113, 3043, and 3166 cal/mol, respectively. From MM3 and *ab initio* calculations, it was shown that the *gauche* conformer of propionyl fluoride had higher barriers to internal rotation of the methyl group than the *gauche* conformers of propionyl chloride or bromide, mainly due to the smaller van der Waals interactions between the halide atom and the methyl group. Still higher barriers to rotation of the methyl group from *ab initio* calculations could be partially explained with torsion-bend interactions, which have not been included in the MM3 force included in the MM3 force field. The experimental barrier to internal rotation of the methyl group of propionyl bromide was expected to be

TABLE VII. Barriers (Calories per Mole) to Internal Rotation of Methyl Group of Acetyl Fluoride, Acetyl Chloride, Acetyl Bromide, Acetyl Iodide, Propionyl Fluoride, Propionyl Chloride, and Propionyl Bromide.

	MW ^a	MW + ED ^b	IR ^c	<i>Ab initio</i> ^d	MM3 ^f
CH ₃ COF	1041(6) ^g	1039 ^h	—	1147 ^e	1042
CH ₃ COCl	1296(30) ⁱ	1260 ^j	—	1287 ^e	1267
CH ₃ COBr	1305(30) ⁱ	1256 ^j	—	1728 ^k	1265
CH ₃ COI	1301(30) ^l	1176 ^h	—	—	1177
CH ₃ CH ₂ COF					
<i>s-trans</i>	2400(60) ^m	—	2670 ⁿ	2743 ^e	2828
<i>gauche</i>	—	—	—	3113 ^e	2404
CH ₃ CH ₂ COCl					
<i>s-trans</i>	2480(80) ^o 2500(50) ^p	—	2440 ^q 2720 ^r	2913 ^e	2863
<i>gauche</i>	—	—	—	3043 ^e	2284
CH ₃ CH ₂ COBr					
<i>s-trans</i>	—	—	2510 ^q 2690 ^s	2308 ^k	2858
<i>gauche</i>	—	—	—	3166 ^k	2242

^aDetermined from the two different energies, *A* and *E* components of the observed doublet of the Q-branch transitions of methyl torsion rotational mode.

^bDetermined in the same way as (a), but by refined analysis using electron diffraction results.

^cThe methyl rotational barrier height was determined from the combination tones, which are the torsional transitions of the methyl group.

^dCalculated by changing dihedral angle, $\omega(\text{H} - \text{C} - \text{C} = \text{O})$ or $\omega(\text{H} - \text{C} - \text{C} - \text{C})$ (in the case of propionyl halides) from 0° to 60° in 10° increment with the optimized structural parameters for the most stable form.

^eCalculated at the RHF / 6-31G* level, using the Gaussian-90 program (in this work).

^fCalculated by changing dihedral angle $\omega(\text{H} - \text{C} - \text{C} = \text{O})$ or $\omega(\text{H} - \text{C} - \text{C} - \text{C})$ (in case of propionyl halides) from 0° to 60° in 10° increment with the optimized structural parameters for the most stable form.

^gTaken from ref. 20.

^hTaken from ref. 24.

ⁱTaken from ref. 22.

^jTaken from ref. 21b.

^kCalculated at the RHF / 3-21G* level, using the Gaussian-94 program (in this work).

^lTaken from ref. 25.

^mTaken from ref. 27.

ⁿTaken from ref. 33.

^oTaken from ref. 28.

^pTaken from ref. 39.

^qTaken from ref. 26b.

^rTaken from ref. 30.

^sTaken from ref. 34.

between our calculated value and the *ab initio*-calculated value.

Conclusion

The newly derived MM3 acyl halide force field showed overall good agreement with the experimental results from a variety of sources, including molecular structures, dipole moments, moments of inertia, and many aspects of energetics including energy barriers and energy differences between different conformers, and energy barriers to inter-

nal rotations over specified bonds. It was also shown that the molecular structures and energetics—for some yet to be determined experimentally—have been predicted by molecular mechanics calculations.

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1. The MM3 program is available to all users from Tripos Associates, 1699 South Hanley Road, St. Louis, MO 63144, and to academic users only from the QCPE, University of Indiana, Bloomington, IN 47405. The calculations described herein might be carried out with the MM3(94) and later

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 - For example, $C_{sp^3}-O-X$ bond parameters (bond types 3-11, 3-12, 3-13, and 3-14), $C_{sp^3}(or\ H)-C_{sp^3}-O-X$ angle parameters (angle types 1-3-11, 1-3-12, 1-3-13, 1-3-14, 5-3-11, 5-3-12, and 5-3-13), $C=O-X$ angle parameters (angle types 7-3-11, 7-3-12, 7-3-13, and 7-3-14), carbonyl out-of-plane bending parameters (angle types 0-3-11, 0-3-12, 0-3-13, and 0-3-14), where X is F, Cl, Br, or I, as well as $C_{sp^3}(or\ H)-C_{sp^3}-C=O$ torsional parameters (torsion angle types 5-1-3-11, 5-1-3-12, 5-1-3-13, 5-1-3-14, 1-1-3-11, 1-1-3-12, 1-1-3-13, and 1-1-3-14) were added into the present MM2 force field.
 - The atom type for $O_{C=O}$ is 7 in MM2. In MM3, the default atom type 7 has been changed to have different atom types according to the source of carbonyl group. For example, the atom type of $O_{C=O}$ of a carboxylic acid, ester, amide, or acyl halide is 77, 78, 79, or 80, respectively, instead of the general atom type 7.
 - In MM3 force fields, the atom types of 1, 2, 22, and 56 have been assigned for default C_{sp^3} , C_{sp^2} , cyclopropane C_{sp^3} , and cyclobutane C_{sp^3} , respectively. The atom type 99 was assigned for $O_{C=O}$ of α,β -unsaturated acyl halides for which atom type 7 as default carbonyl oxygen was assigned in MM2 force fields. So, for cyclopropyl carbonyl halides, cyclopropane C_{sp^3} -cyclopropane $C_{sp^3}-C_{C=O}$ angle parameter (angle type 22-22-3), cyclopropane $C_{sp^3}-C_{C=O}-X$ angle parameters (angle types 22-3-11, 22-3-12, 22-3-13, and 22-3-14), cyclopropane C_{sp^3} -cyclopropane $C_{sp^3}-C_{C=O}-X$ torsional parameters (torsion angle types 22-22-3-11, 22-22-3-12, 22-22-3-13, and 22-22-3-14), and H-cyclopropane $C_{sp^3}-C_{C=O}-X$ torsional parameters (torsion angle types 5-22-3-11, 5-22-3-12, 5-22-3-13, and 5-22-3-14) are required additionally. Likewise, for acryloyl halides, 3-99 bond parameter, 2-3-99 angle parameter, 2-3-11, 2-3-12, 2-3-13, and 2-3-14 angle parameters, 99-3-11, 99-3-12, 99-3-13, and 99-3-14 angle parameters, 2-2-3-11, 2-2-3-12, 2-2-3-13, and 2-2-3-14 torsional parameters, and 5-2-3-11, 5-2-3-12, 5-2-3-13, and 5-2-3-14 torsional parameters are required additionally.
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